

No. 5—INVESTIGATION OF SOME PHOSPHATIC NODULES FROM DANDARAGAN, WESTERN AUSTRALIA.*

BY KEITH R. MILES, D.Sc., F.G.S.

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INTRODUCTION.

The work described in the following pages was carried out consequent upon field investigations of the various phosphatic deposits of the Dandaragan District, conducted by Mr. R. S. Matheson of the Geological Survey of Western Australia during the period May, 1941, to December, 1943.

Specimens used in this investigation included a number of nodules recently collected by Mr. Matheson from pit CG on Cook's Deposit (Upper Phosphate Bed)† located on Melbourne Loc. 704, and nodules (surface boulders) collected from the vicinity of pit BD on Minyulo Deposit (Upper Phosphate Bed) on Melbourne Loc. 284, Dandaragan. Several specimens of phosphatised wood collected by Mr. W. G. Campbell in 1906 from the South-East corner of Melbourne Loc. 957 about five miles north of the principal phosphate deposits on what is now known as "Summer Hill" Deposit (Lower Phosphate Bed), (site of the original find of phosphate rock in the Dandaragan District), were also sectioned and examined.

THE NODULES.

Description.

Four nodules from the Cook's Deposit were sectioned. They were marked A, B, C, and D respectively. It was seen that when broken they ranged from greyish yellow to brownish yellow in colour. The writer was informed by Mr. Matheson that unfortunately most of these nodules were darker in colour and were presumably slightly more ferruginous in composition than the average fresh nodules from Cook's.

The nodules from Minyulo Deposit, being surface boulders were rather weathered, and in places cellular, and coloured a dark brown except where whitened by adhering chalk. One fairly fresh dense and compact-looking specimen was sectioned and marked E. Several other specimens contained partly enclosed fragments of phosphatised wood.

Mega.—On megascopic examination all nodules were found to consist essentially of detrital quartz grains cemented in a fine granular greyish to fawn coloured groundmass. The quartz grains vary in size from fragments up to 5 mm. in diameter down to grains of microscopic size (<0.02 mm.). The average grain size of the quartz varies considerably in different specimens examined, *e.g.*, nodule A contains a much higher proportion of comparatively large grains (>1 mm. diam.) than all other specimens and has an average grain size of about 0.37 mm. In nodules B, C, and D the quartz is more even in grain and has an average diameter of approximately 0.18 mm. Nodule E contains many large grains, though proportionally less than A, and has an average of about 0.26 mm. diameter. The grains range from sub-angular to rounded.

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†Site of the recent find of Mesozoic reptile remains. See Teichert, C., and Matheson, R. S. (6)

In addition to the quartz, nodule A contains a number of clearly visible sub-angular fragments of creamy white colour showing cleavage faces characteristic of *felspar*. These reach up to 3 mm. in diameter.

Broken faces of nodules C, D. and E occasionally contain small cellular surfaces stained yellow with iron oxide.

Micro.—Apart from the detrital quartz and occasional felspar visible in hand specimens as already mentioned, other essential constituents which can be recognised under the microscope are grains of *glauconite* and *iron ore* enclosed in a matrix or cement of light yellow-brown coloured amorphous isotropic material with refractive index distinctly > quartz (about 1.6), which is identified as *collophanite* (or *collophane*). In addition, in many of the slices there are small fragments of phosphatised wood in which the original cell structure is often perfectly preserved but which are now composed entirely of collophanite. The microscopic appearance of typical thin slices is shown in Text fig. 1.

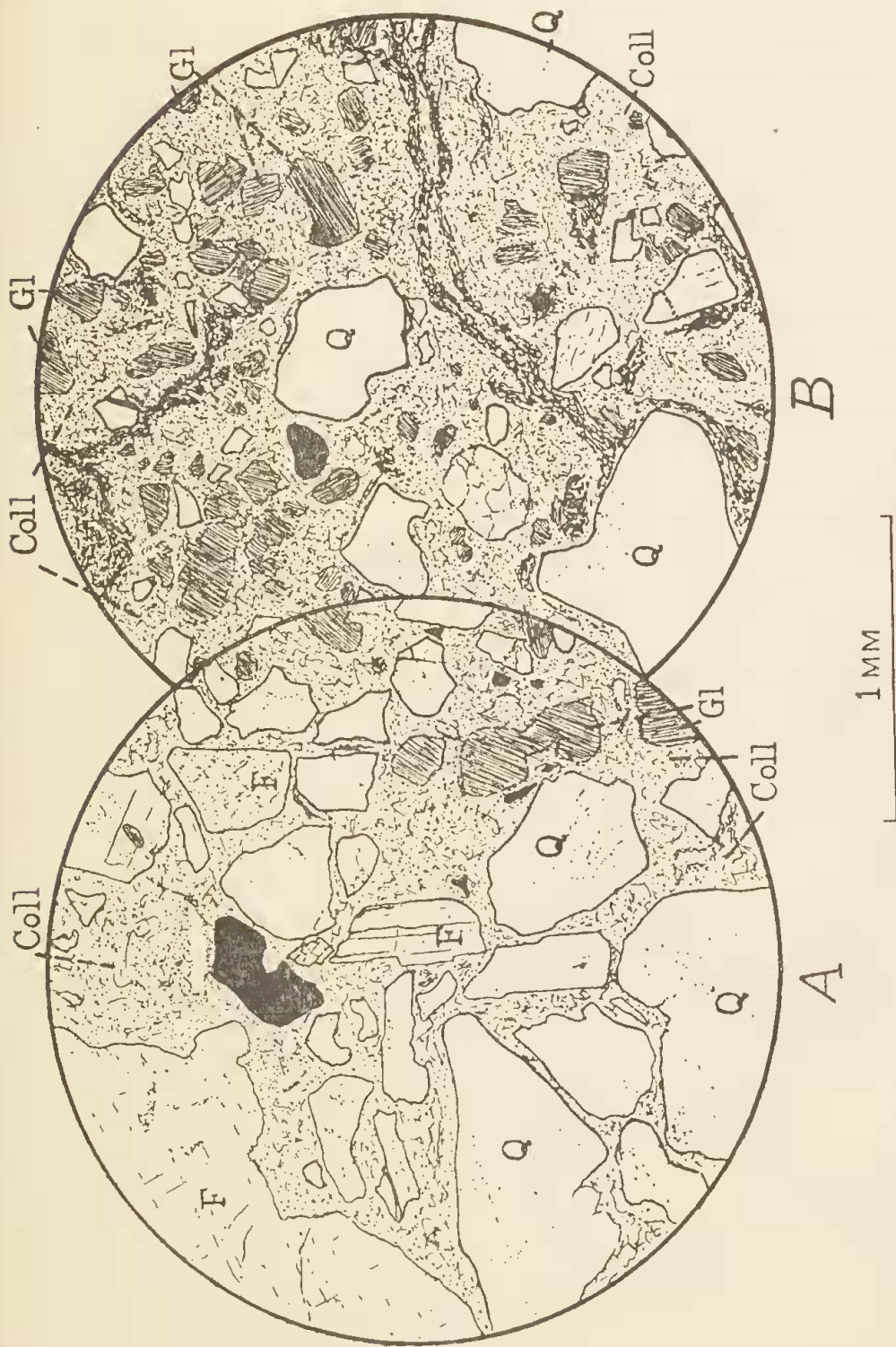
The quartz grains are usually clear and vary from sub-angular and occasionally sharply angular for the smaller grains, to distinctly rounded for the larger grains. A rapid microscopic survey suggests that in nodules containing quartz grains of the same average grain size the degree of rounding is about the same.

Detrital felspar grains were found to be most abundant in nodule A, (Text fig. 1A) but were present in all specimens examined. They consist mainly of *microcline* showing typical cross hatched twinning, but a few grains of untwinned *orthoclase* were recognised. In nodule A both microcline and orthoclase occasionally showed incipient kaolinisation and alteration to pale green chlorite. In nodules B, C, D, and E and to a lesser extent in A, many of the felspar grains showed considerable alteration and replacement along cleavages, to a yellow-green mineral displaying aggregate polarization, which is indistinguishable from the glauconite.

Glauconite is present in varying amount in all specimens. It occurs in irregular shaped rounded pellets or granules ranging in colour from yellow-green to olive green and in size from about 0.03 mm. up to approximately 0.4 mm. diameter (see text fig. 1A and B). These have refractive indices ranging from slightly less than to distinctly greater than that of the enclosing collophanite. They show aggregate polarization, the interference colours being almost entirely masked by the absorption colour of the mineral. No interference figure was obtainable. In several of the nodules, especially in D and E. some of the glauconite showed partial alteration to limonite. Occasionally glauconite granules were seen to enclose minute fragments of black opaque iron ore. The glauconite granules usually occur in scattered groups surrounded by collophanite.

The iron ore occurs in two forms—in sporadically scattered, usually rounded (detrital) black opaque grains ranging from about 0.02 mm. to 0.20 mm. in diameter, and as red opaque filling material found in places rimming grains of glauconite, quartz and black iron ore, and occurring in occasional veinlets traversing the slices.

Examination of the black opaque grains obtained from crushed nodule material showed that some of these were distinctly magnetic and many others non-magnetic and on crushing yield a red powder—thus it is probably mostly *hematite* with some *magnetite*—nearly all grains being altered in some degree at least, to *limonite*.



Textfig. 1.
PHOSPHATE NODULES FROM DANDARAGAN.
A. Nodule A, Cook's Deposit. Showing detrital fragments of quartz (Q), feldspar (F), with several grains of glauconite (Gl) and iron ore—magnetite or hematite (black opaque)—cemented in a matrix of collophanite (Coll). The feldspar grain at top left is portion of a large crystal of microcline.
B. Nodule D, Cook's Deposit. Glauconite (Gl) is much more abundant in this specimen. No feldspar is visible in the field. The collophanite (Coll) matrix is traversed by several vein-like lines which are cloudy and opaque from alteration, and which are slightly stained by limonite.

The red opaque material is *limonite*, obviously a product of weathering and decomposition of other iron bearing minerals in the nodules, *viz.*, glauconite and magnetite-hematite. Although usually concentrated in seams or veinlets, in some of the more weathered specimens the limonite also occurs as a very finely divided material staining the collophanite matrix in irregular patches. In such cases estimation of the relative quantity of limonite present becomes rather difficult.

The collophanite cement where fresh is pale fawn to light yellow-brown coloured and completely isotropic. It is for the most part massive and structureless except where it has replaced fragments of woody tissue or where, particularly surrounding quartz grains and vugs in nodule A, it displays distinct colloform structures. Under high powers apparently clear collophanite is seen to be filled by microscopic inclusions in which limonite, glauconite and gas bubbles can be recognised. Under high powers the colloform areas in nodule A and to a lesser extent in B, D, and E, reveal crusts with banded subradiating structure, of a pale grey coloured very weakly birefringent mineral. This has straight extinction. Columns of crusts are sometimes length slow and sometimes length fast so that though some of this may be collophanite it is probably in part the secondary *dahllite*, or *francolite*, or a related mineral.

In the more weathered portions of specimens examined the collophanite matrix is usually altered to a red-grey cloudy opaque material often heavily stained with limonite.

Accessory detrital minerals noted were zircon in rare broken grains in nodules E, A, and B and one or two grains of rutile and pink garnet in A. It may be noted here that no calcium carbonate minerals and no iron or aluminium phosphates were seen in any of the slices examined.

Relative Composition.—To determine the approximate mineral composition of the phosphate nodules micrometric analyses were made of four specimens—A, B, and C from Cook’s Deposit and nodule E from Minyulo. The results of these analyses are set out in the following table :—

TABLE 1.
APPROXIMATE MINERAL CONTENT OF PHOSPHATE NODULES.

Mineral.	Cook’s Deposit.				Minyulo Deposit.
	Nodule A.	Nodule B.	Nodule C.	Average.	Nodule E.
	%*	%	%	%	%
Quartz ...	55½	24½	17	32½	42
Collophanite ...	31½	45½	61½	46	32
Glauconite ...	4½	20	13	12½	15
Iron Ore ...	3½	7	6	5½	9
Felspar ...	5	3	2½	3½	2
	100	100	100	100	100

* All percentages are by weight.

In carrying out the micrometric measurements, the author probably tended to overestimate the iron ore, especially limonite—particularly in the more weathered specimens B, C, and E—since he was inclined to class brownish, iron-stained glauconite granules as wholly limonite at times, and it is considered that the figures for iron ore shown above may be a little high.

No attempt was made to differentiate between the magnetite-hematite and the limonite which in most specimens are in the ratio of between 1:2 and 1:3. In calculating the relative weights the following specific gravities were used; quartz 2.65, collophanite 2.7, glauconite 2.6, iron ores 4.5, felspar 2.55. Phosphatised wood fragments were included with the matrix when measuring the collophanite content. Felspar was estimated as microcline. The accessory minerals were neglected.

From Table I it can be seen that the relative proportions of the three main constituents quartz, collophanite and glauconite vary considerably between wide limits, though quartz and collophanite appear to occur in inverse ratio one with the other. The fact that the total glauconite, iron ore and felspar content is appreciable in all specimens examined, indicates that notable amounts of iron oxide and alumina are present in the nodules.

In Column 4 of Table I is given the average composition of nodules A, B, and C from Cook's Deposit. Then assuming the following approximate compositions for the minerals; glauconite SiO_2 52%, Fe_2O_3 20%, Al_2O_3 10%, MgO 3% (1) and K_2O 3% (2); iron ore Fe_2O_3 85%; and felspar SiO_2 65%, Al_2O_3 18%, K_2O 16% (3); the Cook's Deposit nodules have the approximate partial chemical composition shown in Column 1 of Table II.

No attempt has been made to estimate the CaO and P_2O_5 content, etc., as the exact composition of collophanite (essentially hydrous calcium phosphate with variable amounts of calcium carbonate, fluoride and sulphate, etc.), is not known.

The above figures bear interesting comparison with the results of a complete chemical analysis of a composite sample of nodules from Cook's Deposit made at the Government Chemical Laboratory shown in Column 2 of the following table:—

TABLE II.
ANALYSIS OF NODULES.

	1.	2.
	%	%
SiO_2	40.6	46.02
Al_2O_3	1.8	2.36
Fe_2O_3	7.1	3.38
MnO	0.02
MgO	0.36	0.42
CaO	23.62
K_2O	0.85	0.80
P_2O_5	16.66
CO_2	1.70
$\text{H}_2\text{O} +$	1.29
$\text{H}_2\text{O} -$	0.98
SO_3 (water soluble)	0.04
SO_3 (acid soluble)	0.15
Cl	0.01
F	Present
Loss on Ignition	0.41
	98.09

1. Micrometric analysis showing partial composition of average of three nodules from Cook's Deposit. All percentages shown are by weight. (Anal. K. R. Miles).
2. Chemical Analysis of a composite sample of nodules from Cook's Deposit. (Anal. H. P. Rowledge).

Comparison of these figures tends to bear out the impression that the specimens examined by the author contain appreciably more iron oxide (probably in the form of iron ores) than the average nodules from Cook's Deposit but it is interesting to note that probably *all* iron oxide, alumina, potash and magnesia shown in the chemical analysis of the composite sample *can be accounted for by the glauconite, iron ore and felspar in the nodules themselves.*

THE PHOSPHATISED WOOD.

An examination was made of thin slices of three specimens of phosphatised wood. Some of this material was figured and described by Simpson in 1912 (4). The "wood" itself is now completely replaced by phosphatic material optically and microscopically indistinguishable from the collophanite (which Simpson regarded as fluorapatite) matrix of the nodules described above except that in most cases the minute structures of the original woody tissue have been perfectly preserved. The wood has been identified as a Mesozoic conifer classed as *Cedroxylon* (4).

Of interest in the present investigations is the fact that all the specimens examined are abundantly riddled with tunnels and pipes filled with phosphatic material which appears identical in composition with the phosphatic nodules already described. These tunnels are considered to have been made by boring organisms in the original wood. Specimens of wood examined ranged from $1\frac{1}{2}$ inches to 3 inches in diameter and were up to $3\frac{1}{2}$ inches long. The borer holes are up to about 0.35 inch in diameter and often run the full length of the wood specimen.

Under the microscope the material filling these borer holes is seen to consist essentially of detrital quartz and felspar, and abundant glauconite with rare scattered fragments of black opaque iron ore (? magnetite) set in a matrix of collophanite similar to that found in the phosphate nodules. Some secondary limonite was seen in the more weathered specimens but was completely absent from the freshest specimen examined.

The quartz in this material is fine and even grained, seldom more than 0.5 mm. in diameter. The felspar includes fragments of microcline, orthoclase and twinned plagioclase, probably oligoclase. Detrital zircon is a rare accessory. In addition to the above, the borders of several borer holes were marked by clusters of tiny spherical brown bodies. These have already been noted by Simpson (*op. cit.*) and considered to be the fossil excreta of wood boring beetles.

No attempt was made to measure the relative proportions of the components of the filling material in these borer holes, but from a visual inspection the writer considers that although the iron ore content is probably less than that of nodule A described above, the average glauconite content is at least as high as in nodule E and is probably between 15 to 20 per cent. The proportion of quartz to felspar is probably about 10 : 1.

It is interesting to note therefore that even in specimens of phosphatised wood, which from Dandaragan is a source of high grade phosphate, there is a certain amount of deleterious material (iron oxide and alumina) present in the form of minerals occurring as filling material for the numerous borer holes within the wood.

ORIGIN OF THE NODULES.

In his original description of the Dandaragan phosphate deposits in 1907 W. D. Campbell (5) stated that the phosphate nodules were "coprolites," presumably accumulations of animal excreta, bones and teeth. Simpson's subsequent investigations in 1912 (4) showed that the so-called bones and teeth were in reality fossil wood, and it was not until December, 1943, that undoubted bone fragments were recognised and identified from these deposits (6). Simpson seems to have retained the term "coprolite" for the nodules, however, and this name apparently remained unchallenged until the last few years. As a result of field investigations in the Dandaragan District in 1941 Matheson in an as yet unpublished report (7) expressed the view that the nodules are of inorganic origin and quoted the supporting opinion of Teichert that the use of the term 'coprolite' bed should be discontinued.

Evidence available from the present investigation is, in the writer's opinion, strongly in favour of the view that these nodules have been formed by inorganic chemical action. The nodules are composed of grains of quartz, glauconite, felspar and iron ore—all normal components of the enclosing greensand—which are cemented together by phosphatic material to form separate rounded, relatively compact bodies lying within beds of more or less consolidated glauconite, quartz, felspar, etc., grains intermixed with some chalk. This suggests that nodules have been formed by deposition of calcium phosphate (collophanite) around grains of quartz, glauconite, etc., within the original greensand, and that gradual accumulation about these primary centres of deposition has resulted in larger and larger concretions. It is probable that in many cases original interstitial chalk has been replaced by the cementing calcium phosphate, whilst the frequent presence of phosphatised wood fragments within the nodules themselves suggests that wood fragments have often formed the nuclei for the growth of nodules.

No clue as to the source of the original phosphoric acid responsible for the precipitation of the collophanite was afforded by this microscopical investigation of the nodules, though it may be hazarded that this material was probably dissolved out of original organic remains either from within the enclosing beds or from an adjacent, possibly higher horizon.

SUMMARY AND CONCLUSIONS.

A number of specimens of phosphatic nodules from Cook's Deposit, and one from Minyulo Deposit, Dandaragan, have been examined microscopically and their mineral content figured and described. Unfortunately the material available for examination from both deposits is probably not truly representative but is slightly more ferruginous than the average nodules.

Micrometric analyses were made to determine the relative proportions of the essential minerals present, *viz.*, quartz, collophanite, glauconite, iron ore and felspar, in several specimens, and the results tabulated. All specimens contained appreciable quantities of glauconite, iron ore and felspar.

Taking the average mineral composition of specimens from Cook's Deposit, the partial chemical composition was calculated. These figures were compared with those of a complete chemical analysis of a composite sample of nodules from Cook's Deposit, and they showed tolerably good agreement.

As a result of this investigation it can be said that most if not all of the iron oxide and alumina obtained from chemical analyses of coarser fractions from sizing tests of Dandaragan phosphate rock occur within the nodules

themselves, as the minerals glauconite, magnetite, hematite, or limonite, and felspar, and not in any outside coating material. No calcium carbonate in crystalline form was recognised during microscopic examination of the nodules though it is possible that a little may be present as a decomposition product of the collophanite. A certain amount of calcium carbonate in the form of chalk is present as a coating on the nodules.

A number of specimens of phosphatised wood (high grade phosphate) from Dandaragan were also examined microscopically. All specimens contained borer holes filled with lower grade phosphatic material similar in mineral composition to the phosphate nodules, *i.e.*, containing *inter alia* a certain amount of iron oxide and alumina as glauconite, iron ore and felspar.

The mineral composition and microstructure of the nodules point clearly to their inorganic origin and they are believed to have formed by precipitation of calcium phosphate about mineral grains in the original greensand. Phosphatised wood fragments have often provided nuclei for the accretion of phosphatic material and the growth of nodules.

ACKNOWLEDGMENTS.

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